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An unusual cascade reaction of 4,5-dihydro-4,4-bis(trifluoromethyl)-2-phenyl-6,7-(4-chlorobenzo)[*e*]-1,3,2-dioxaphosphepin-5-one with chloral

Vladimir F. Mironov,*[a,b] Yuliya Yu. Borisova,[a] Liliya M. Burnaeva,[a] Dmitry B. Krivolapov,[b] Igor A. Litvinov,[b] Vladislav V. Zverev,[b] Rashid Z. Musin[b] and Irina V. Konovalova[a]

[a] *A. M. Butlerov Chemical Institute, Kazan State University, 420008 Kazan, Russian Federation. Fax: +7 843 231 5416; e-mail: liliya.burnaeva@ksu.ru*
[b] *A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 843 273 1872; e-mail: mironov@iopc.kcn.ru*

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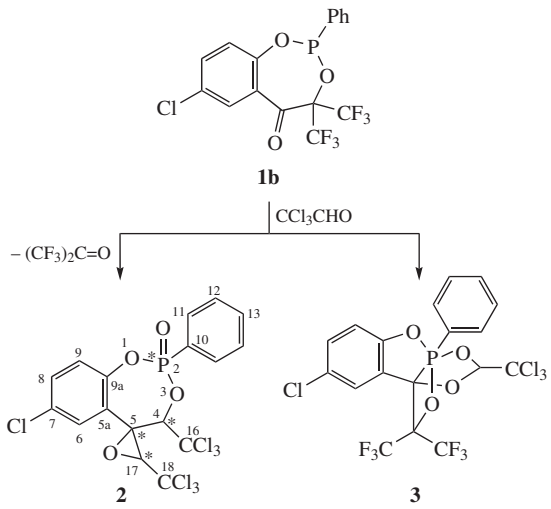
The reaction of 4,5-dihydro-4,4-bis(trifluoromethyl)-2-phenyl-6,7-(4-chlorobenzo)[*e*]-1,3,2-dioxaphosphepin-5-one with chloral (1:2) proceeds with evolving hexafluoroacetone and gives spiro{2-oxo-4-trichloromethyl-4,5-dihydro-2-phenyl-6,7-(4-chlorobenzo)[*f*]-1,3,2-dioxaphosphepine-5,2′-(3′-trichloromethyl)oxirane} with a high stereoselectivity. Configuration of the four chiral centres ($P^2_SC^4_SC^5_SC^{3'}_S/P^2_RC^4_RC^5_RC^{3'}_R$) was determined by a single crystal X-ray diffraction.

The reactions of P^{III} derivatives with carbonyl compounds are important for the synthesis of compounds bearing pentacoordinated phosphorus, which are the intermediates in the nucleophilic displacement reaction at tetracoordinated phosphorus species.[1–6] Recently,[7,8] we found that the reaction of $\lambda^3\sigma^3$-1,3,2-dioxabenzophospholes having a γ- or δ-carbonyl group to the phosphorus atom in exocyclic substituent leads to the formation of 'carcass' phosphoranes. In spite of the formation of a few chiral centres, the process has a high regio- and stereoselectivity. The reaction was also applied to the P^{III} derivatives bearing γ-endocyclic carbonyl group relative to the phosphorus atom, such as 4,5-dihydro-4,4-bis(trifluoromethyl)-2-phenyl-6,7-benzo[*e*]- and 4,5-dihydro-4,4-bis(trifluoromethyl)-2-phenyl-6,7-(4-chlorobenzo)-[*e*]-1,3,2-dioxaphosphepin-5-ones **1a**,**b**. The 5-carbaphosphatrane derivatives with pentacoordinated phosphorus atom, containing three oxygen atoms in equatorial sets and two less apicophilic carbon ones in apical sets were unexpectedly obtained in the reaction of compounds **1a**,**b** with hexafluoroacetone.[9]

In this work, we attempted to use chloral as another reactive compound for the synthesis of 5-carbaphosphatranes. However, the interaction of chloral with dioxaphosphepine **1b** is more complex and proceeds by two main directions. The first direction leads to the formation of the unusual derivative with tetracoordinated phosphorus atom – spiro{2-oxo-4-trichloromethyl-4,5-dihydro-2-phenyl-6,7-(4-chlorobenzo)[*f*]-1,3,2-dioxaphosphepine-5,2′-(3′-trichloromethyl)oxirane} **2**. The evolving of hexafluoroacetone, detected owing to the characteristic odour, took place in the course of the reaction. The content of compound **2** in the reaction mixture is about 70%.† The second direction involves the formation of 5-carbaphosphatrane derivative **3** as a minor compound.

The stereoselectivity of the formation of product **2** is very high. In spite of three additional asymmetric centres, only one diastereoisomer was formed and isolated in view of crystals suitable for X-ray diffraction (as a solvate with one CH_2Cl_2 molecule).‡ The molecular geometry of compound **2** is shown in Figure 1. The phosphorus atom has a distorted tetrahedral configuration, a seven-membered heterocycle has a distorted boat conformation and includes the planar four-atoms fragment C(5)C(5a)C(9a)O(1), the atoms P(2), O(3) and C(4) being situated on one side and at various distances of the latter. Phenyl and trichloromethyl substituents, as well as oxirane carbon atom [C(11)], are in pseudo-equatorial sets, the phosphoryl oxygen and the oxirane cycle



Scheme 1

† Solvents and commercial reagents were purified by conventional methods before use. All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. Measurements involved a Boetius melting point apparatus. NMR experiments were performed in $CDCl_3$ at 20 °C with Varian Unity-300 (^{31}P, ^{31}P-{^{1}H} at 121.42 MHz; ^{19}F at 282.4 MHz) and Bruker Avance-600 spectrometers with a 5 mm diameter inverse probe head with Z-active shielded gradients working at 600 MHz for ^{1}H and 150.864 MHz for ^{13}C. The δ_H and δ_P values were determined relative to internal (HMDS) or external (H_3PO_4) standard. The δ_F values were determined relative to internal standard (C_6F_6) and then re-calculated relative to $CFCl_3$. The δ_C values were determined relative to the deuterated solvent signal. IR spectra were recorded on a Specord M-80 instrument in Nujol. EI mass spectra were obtained with a TRACE MS Finnigan MAT instrument; the ionization energy was 70 eV and the ion source temperature was 200 °C. The samples were introduced into the ion source *via* a direct inlet system. The evaporating ampoule was heated from 35 to 150 °C at a rate of 35 K min^{-1}. The mass spectrometric data were processed using the Xcalibur system program.